AN INVESTIGATION OF THE INFRARED SPECTRA OF THE RARE EARTH ACETYLACETONATES AND OXALATES

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Master of Arts

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by

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CHAPTER I

THE PROBLEM AND ITS IMPORTANCE

The use of various ligands for the group separation of the rare earth elements (lanthanides) has been known for some time. For example, lanthanides as a group are separated by the precipitation of their oxalates. In addition, the use of acetylacetone to precipitate the insoluble lanthanide acetylacetonates has been proposed. However, very little work has been done with these acetylacetonates because of their great tendency to decompose on strong heating (1). Even less is known about the structure of these complexes.

I. THE PROBLEM

Statement of the problem. The purpose of this study was (1) to prepare the individual pure lanthanide oxalates and acetylacetonates, (2) to obtain, and analyze the infrared absorption effects in the 600-4000 cm^{-1} region with respect to frequencies and relative intensities, (3) to interpret these effects in terms of metal-ligand bonding, and hopefully , (4) to develop a qualitative and quantitative method for determining the lanthanides based on infrared spectrometry.

Importance of the problem. To characterize the structure of the lanthanide complexes, it is necessary to obtain information about the nature of the metal-ligand bonding. For example, it is of importance to see what effect ionic size and the type of hybridization has on the metal-ligand bonding.

From a practical standpoint, variations in the infrared absorption band frequencies might correlate with the nature of the particular lanthanide. This, hopefully, could form the basis for a rapid and non-destructive method of qualitative and quantitative analysis of the rare earths based on infrared spectroscopy.

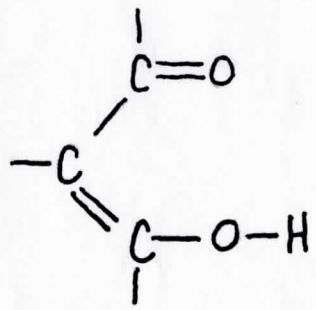
CHAPTER II

REVIEW OF THE LITERATURE

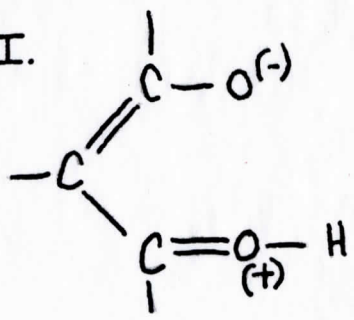
I. ACETYLACETONE COMPLEXES

A number of studies of acetylacetone complexes of metals other than the rare earth elements have been reported (2) (3) (4) (5) (6) (7) (8) (9) (10) (11) (12). Astbury (2) determined the structure of the acetylacetone complexes of Al, Cr, Mn, Co, Ga, Sc, and In by x-ray diffraction. He found the stability to be the result of chelation of three acetylacetone groups about the metal ion in an octahedral complex. Later, Lecomte (3) studied complexes of Be, Cr, Fe, Cu, Zn, Th and U by infrared spectroscopy. It was concluded that the complexes were cyclic, that spectral band changes due to metal changes occurred in the 600-700 cm^{-1} region, and that the metal was present as a complex rather than a salt. Duval, et. al. (5) in a similar investigation confirmed Lecomte's conclusions. They suggested that the metal-oxygen bond perturbed the carbonyl vibration and considered enol and keto forms to exist in acetylacetone. However, they found no band in the carbonyl region (1710-1730 cm^{-1}). Bellamy, et. al. (13), however, placed this band at 1724 cm^{-1}. They propose that the enol chelate band should occur at 1608 cm^{-1} in acetylacetone. The structures below were proposed.

I.



II.



Holtzclaw, et. al. (8) studied the acetylacetone complexes of Pd, Mn, Cd, Cr, (III), Fe (III), Ni (III), Mg, Al, and Na. They concluded that the carbonyl band position was related to the masses of groups attached to the ends of the ligand, the interaction of the carbonyl group with neighboring π or d orbitals, and the relative density of the σ bond. It was suggested that the mass of the metal ion had very little influence on the strength of the metal-oxygen bond. Therefore, the metal-oxygen bond length should be independent of the shape of the complex.

In a later study, (9) theoretical calculations of the frequencies to be expected for Cu (II) acetylacetonate were made and compared with observed values. These are given in Table I. From this analysis, it was concluded that the copper-oxygen bond had double bond character, the 1580 cm^{-1} band was an asymmetric C=C bond, and the 684 cm^{-1} and the 654 cm^{-1} bands were metal-oxygen stretching vibrations and C—CH_3 bending modes, respectively. Table II gives the results of a similar analysis (10). In Table II band assignments are given for acetylacetone complexes of Co (III), Fe (III), Al, and Cu (II). (10).

II. OXALATE COMPLEXES

The earliest infrared study of oxalate complexes was that of Douville et. al. (11). These investigators concluded that a resonance effect occurred between the two oxygen atoms attached to the same carbon atom. This type of resonance was considered to be similar to that in nitrogen dioxide and carbon dioxide. No normal carbonyl band (1700-1800 cm^{-1}) was reported. In their analysis of the spectra, deformation modes occurred between 800 and 950 cm^{-1} and rotation was shown in the 600 to 775 cm^{-1} region.

TABLE I

BANDS OBSERVED AND CALCULATED FOR
COPPER II ACETYLACETONATE

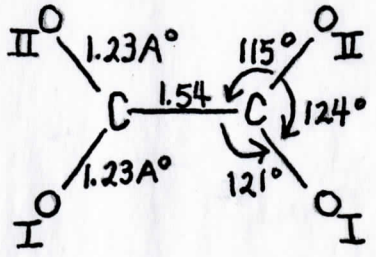
	Observed Wavenumbers	Calculated Wavenumbers
(symmetric) A	1554	1566
	1274	1251
	937	934
	684	657
(asymmetric) B	1580	1594
	1534	1500
	1190	1225
	937	881
	654	631
	1415	
	1356	
	1020	
	781	
	614	

TABLE II

OBSERVED AND CALCULATED BANDS (IN WAVENUMBERS) OF SEVERAL ACETYLACETONATES WITH THEIR CORRESPONDING BAND ASSIGNMENTS

Cobalt (III)		Iron (III)		Aluminum (III)		Copper (II)		Predominant Modes
Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	
1578	1576	1572	1575	1590	1590	1580	1580	C=C str
1527	1532	1526	1529	1545	1548	1554	1544	C=O str
				1530		1534		
1430	1480	1425	1477	1466	1487	1464	1489	CO str and CH bend
1390		1390		1387		1415		CH_3 deg def
1372		1365		1387		1356		CH_3 sym def
1284	1263	1276	1262	1288	1250	1274	1264	CC str and CCH_3 str
1195	1224	1190	1221	1191	1222	1190	1226	C—H in plane bend
1022		1022		1028		1020		CH_3 rock
934	936	930	926	935	939	937	936	CCH_3 + CO str
	902		895		885		901	CCH_3 str
780				773		781		C—H out of plane bend
771								
764								
691	671		648	685	675	684	659	Ring def and M—O str
671	641		602	658	645	654	628	C—CH_3 bend and M—O str
672								
662								
633								

An x-ray analysis of the oxalate ion (14) showed the ion to be planar with bond angles and distances shown below.



In later studies, Fujita, et. al. (12) investigated the oxalates of Al, Co (III), Cr (III), Fe (III), Cu (II), Co (III) and Ni (II). From this study, it was concluded that the metal-ligand bond becomes stronger or weaker. In addition, the fundamental vibrations of the ligand became stronger or weaker and shifted to higher or lower frequencies due to differences in bond strength. It was found that the carbon-oxygen II bond shortened as the metal-oxygen bonds become stronger. These workers reported that the metal-oxygen bond should shorten in the following order: Ni (II) (weakest bond), Co (II), Cu (II), Fe (III), Cr (III), and Al (III) (strongest bond).

CHAPTER III

EXPERIMENTAL

I. PREPARATION OF LANTHANIDE ACETYLACETONATES

The method for preparing the acetylacetonates was the one suggested for preparing thorium acetylacetonate (15). The original preparation was scaled down for the present work since only small quantities were needed for the infrared analysis. The acetylacetone complexes of La, Ce, Pr, Nd, Sm, Gd, Dy, Ho, Er, and Yb were prepared.

The general procedure used for preparing these complexes consisted of suspending 5 grams of freshly distilled acetylacetone in 10 ml. of distilled water. 6 N ammonium hydroxide was then added drop-wise from a buret until solution was effected. This solution was next added to a solution composed of 5 grams of the rare earth nitrate dissolved in 40 ml. of distilled water. Upon combination of the solutions the complex precipitated. The precipitate was made alkaline to litmus with 6 N ammonium hydroxide, filtered, washed with distilled water, then air-dried (15). The complexes were air dried several days, then bottled for future analysis.

II. PREPARATION OF THE RARE EARTH OXALATES

All of the rare earth oxalates were obtained from City Chemical Corporation in 99.9% purity except lanthanum and cerium. The oxalates of La and Ce were prepared by this worker. These oxalates were prepared by the method suggested by Pearce, et. al. (16). Lanthanum chloride and cerium

nitrate obtained from Fisher Scientific Company (99% purity) were dissolved, in turn, in water and a 60°C solution of saturated oxalic acid was added. Upon addition of the two solutions, the rare earth oxalate precipitated. The precipitate was filtered, washed, then air dried, and finally bottled for future analysis.

III. INFRARED ANALYSIS OF THE LANTHANIDE COMPLEXES

Infrared spectra were obtained for acetylacetone, oxalic acid and the acetylacetonates and oxalates of La, Ce, Pr, Nd, Sm, Gd, Dy, Ho, Er, and Yb.

All samples investigated were in the form of potassium bromide pellets except the acetylacetone. This was a 10% solution of acetylacetone in carbon tetrachloride.

The potassium bromide pellets of the various lanthanides were prepared by the same method so as to have the same thickness and the same quantity of material in each pellet. The method used for preparing the pellet consisted of grinding analytical grade potassium bromide to a very fine powder in an agate mortar. The ground sample was transferred to a beaker, and dried in an oven at approximately 100°C. 0.5 gram of the dried KBr was mixed thoroughly with 2 mg. of the rare earth complex. The mixed sample was then placed in the die and a small amount of pressure was applied. A vacuum was applied to the die throughout the pressing process. Approximately two minutes after applying the vacuum, the pressure on the sample was increased to 21 psig and maintained constant for from 10 to 15 minutes. The pellet was removed, then placed in the sample holder of the Beckmann Infrared Spectrophotometer, IR-7.

Infrared spectra for each of these samples were obtained with the

spectrophotometer in the region from 600 cm^{-1} to 4000 cm^{-1}. In obtaining these spectra optimum operation conditions of slit width, period, scanning speed, chart speed, and gain were used in double beam operation.

Each of these spectra were indexed with respect to frequencies and relative intensities and compared for differences in these structural parameter.

CHAPTER IV

RESULTS AND DISCUSSION

In Figure 1, the infrared spectrum of acetylacetone is shown. The absorption band frequencies and relative intensities are listed in Table III. Figures 2, 3, 4, 5, 6, 7, 8, 9, 10, and 11 show the spectra of the acetylacetonates of La, Ce, Pr, Nd, Sm, Gd, Dy, Ho, Er, and Yb, respectively. The absorption bands for the La, Ce, Pr, Nd, Sm, Gd, Dy, Ho, Er, and Yb complexes (acetylacetonates) are listed in Table III. A comparison of the absorption bands of acetylacetone with the absorption bands of the various lanthanide acetylacetonates show differences which are associated with the combination of acetylacetone with the metal ion. However, when the bands for the various complexes are compared with each other, no significant differences in frequencies are observed. This finding suggests that the metal-ligand bond is insensitive to the changes in the mass of the central metal ions. Some changes in intensity were observed for some of the complexes. It is suggested that these intensity changes may be related to the crystal morphology of the complex.

The infrared spectrum of oxalic acid is shown in Figure 12. The absorption bands are given to Table III. Figures 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, and 23, are the spectra of the oxalates of La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, and Yb, respectively. The absorption bands are listed for these oxalates in Table III also. Similar observations can be made about the similarity of the bands for the various lanthanide oxalates. It is suggested that the metal-oxygen bond strength is insensitive to change in the mass

of the central ion. In Table IV the band assignments of the cerium oxalate and acetylacetonate are suggested. These are based on comparison of these complexes with similar complexes of the transition metals.

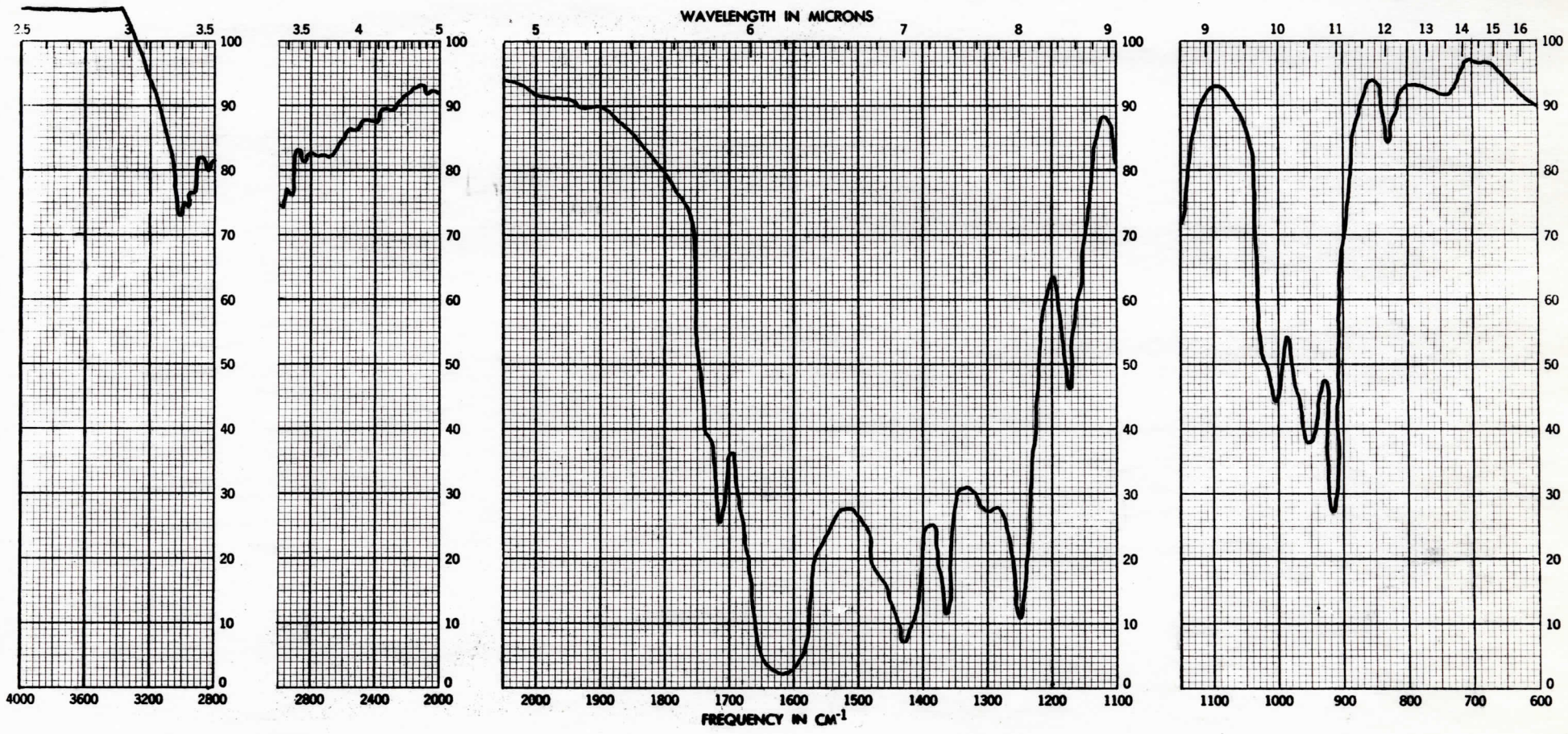


FIGURE 1

SPECTRUM OF ACETYLACETONE

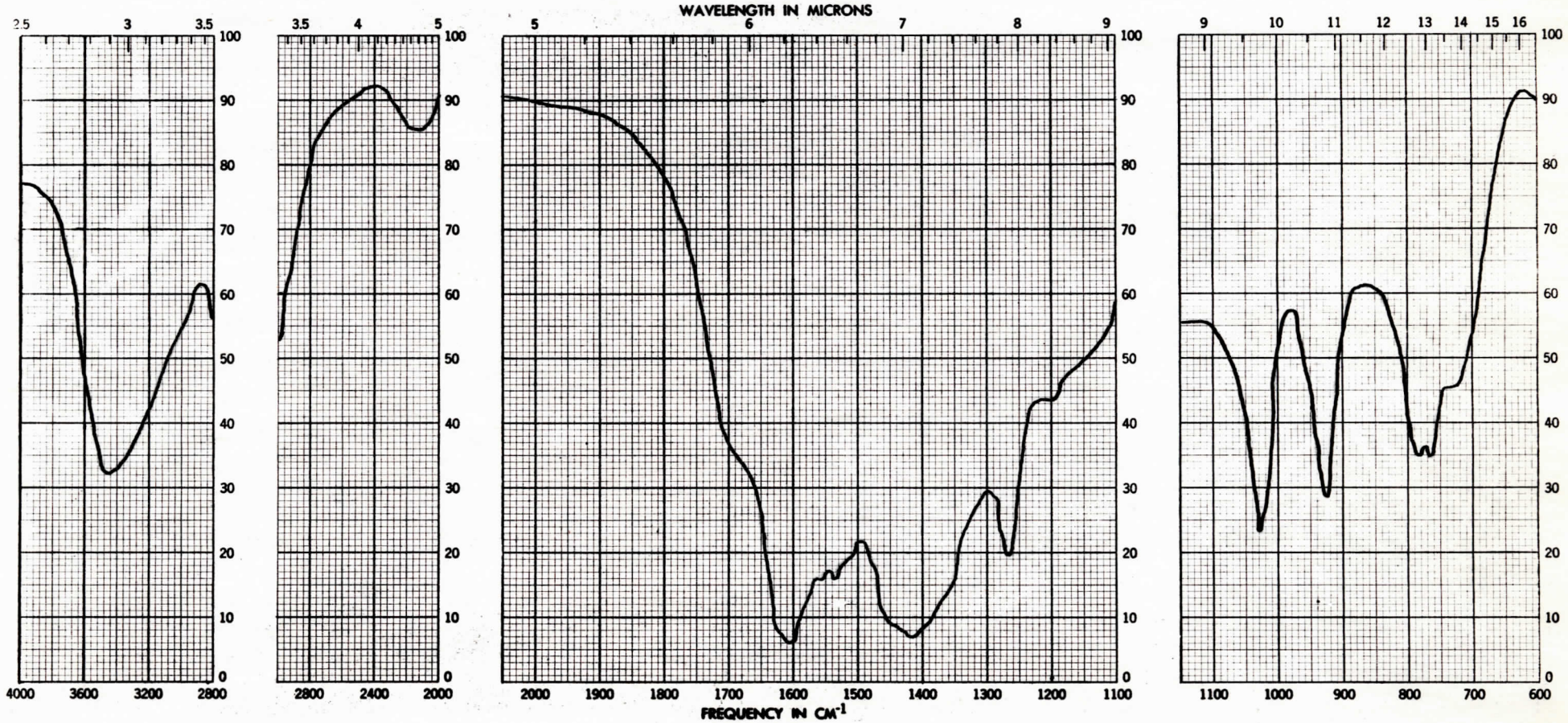


FIGURE 2

SPECTRUM OF LANTHANUM ACETYLACETONATE

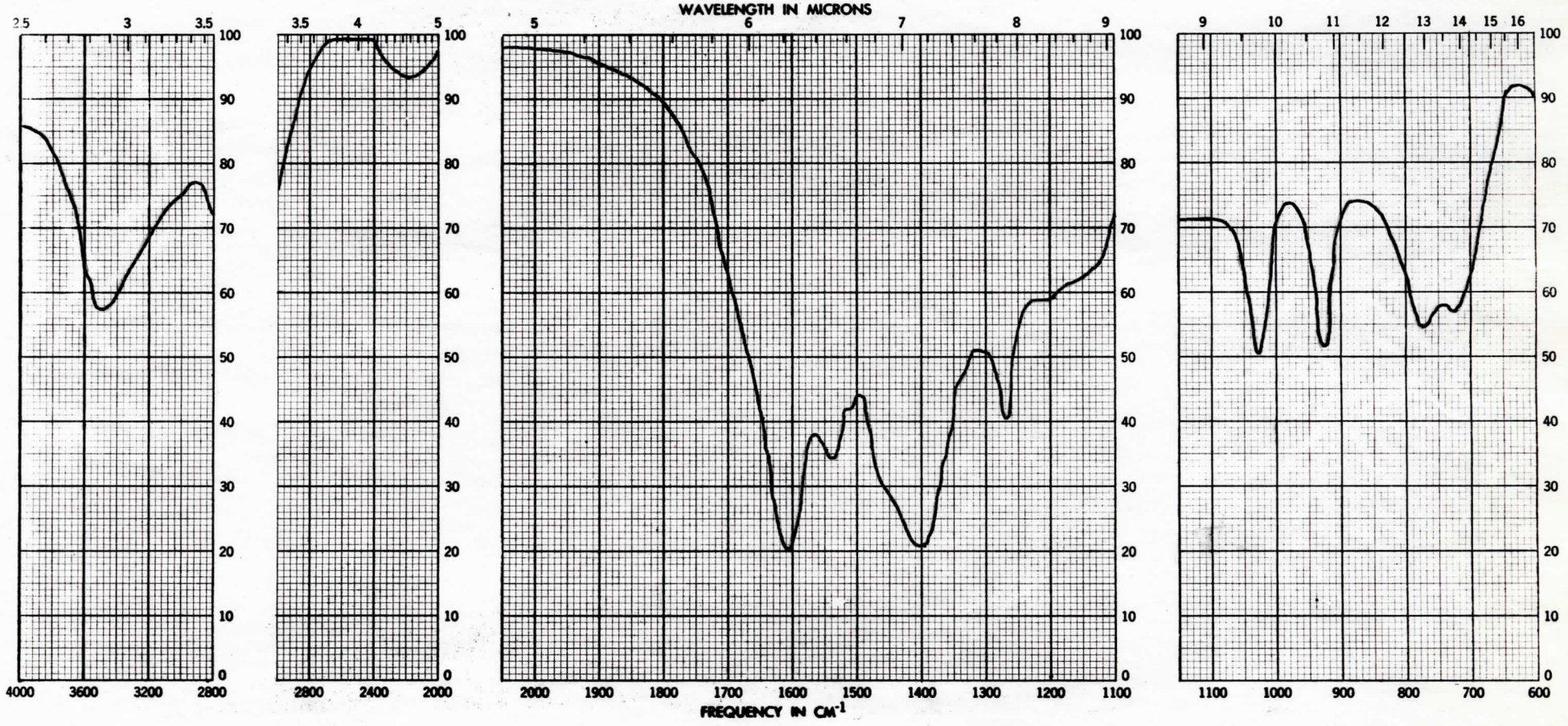


FIGURE 3

SPECTRUM OF CERIUM ACETYLACETONATE

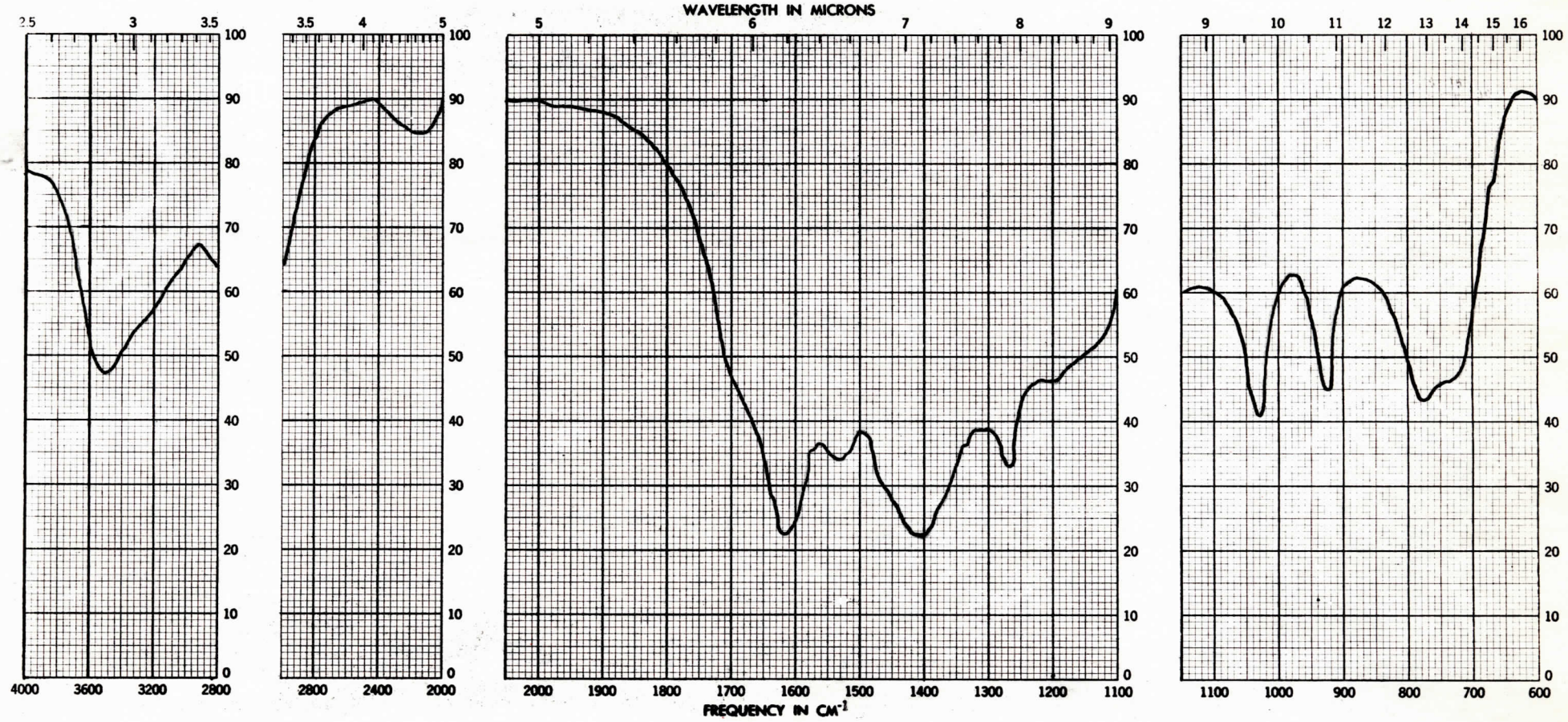


FIGURE 4

SPECTRUM OF PRASEODYMIUM ACETYLACETONATE

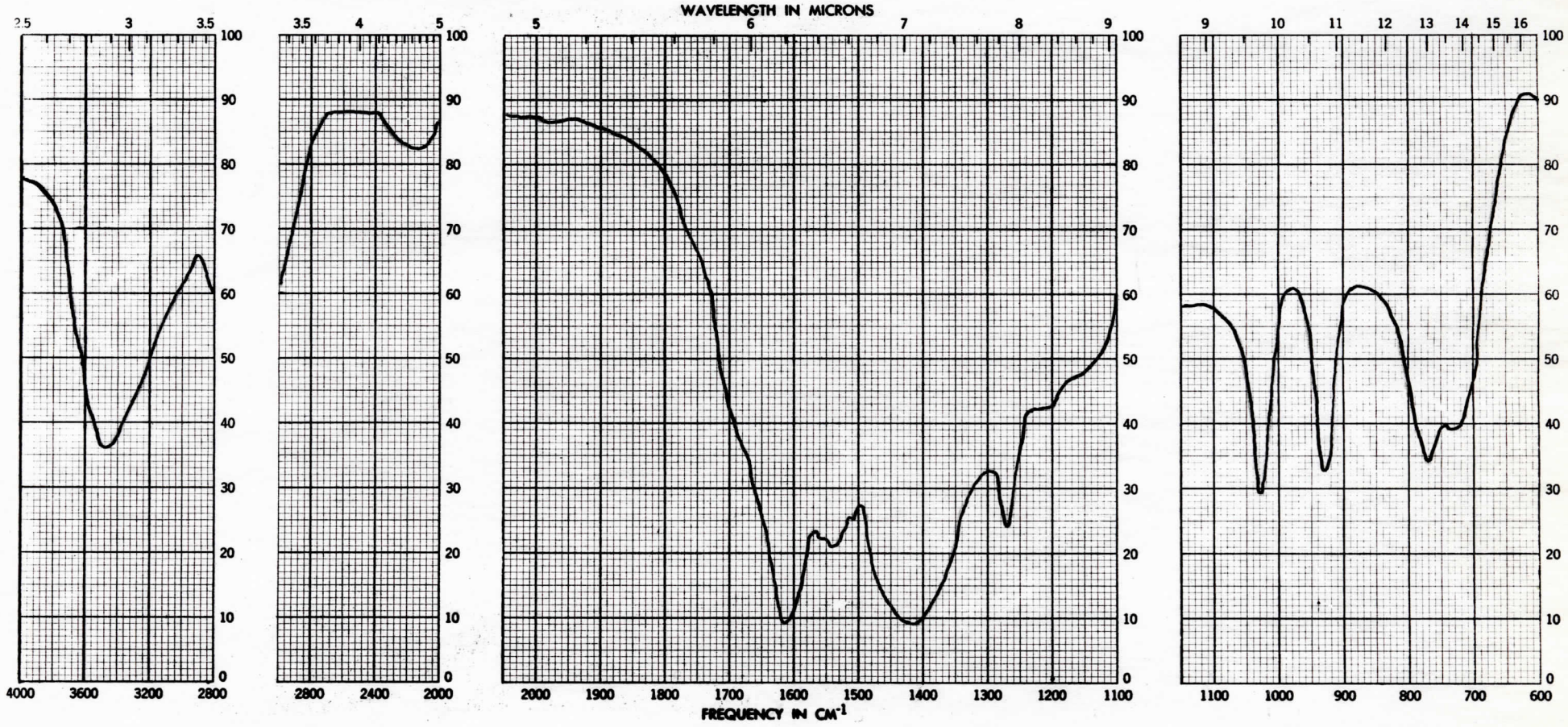


FIGURE 5

SPECTRUM OF NEODYMIUM ACETYLACETONATE

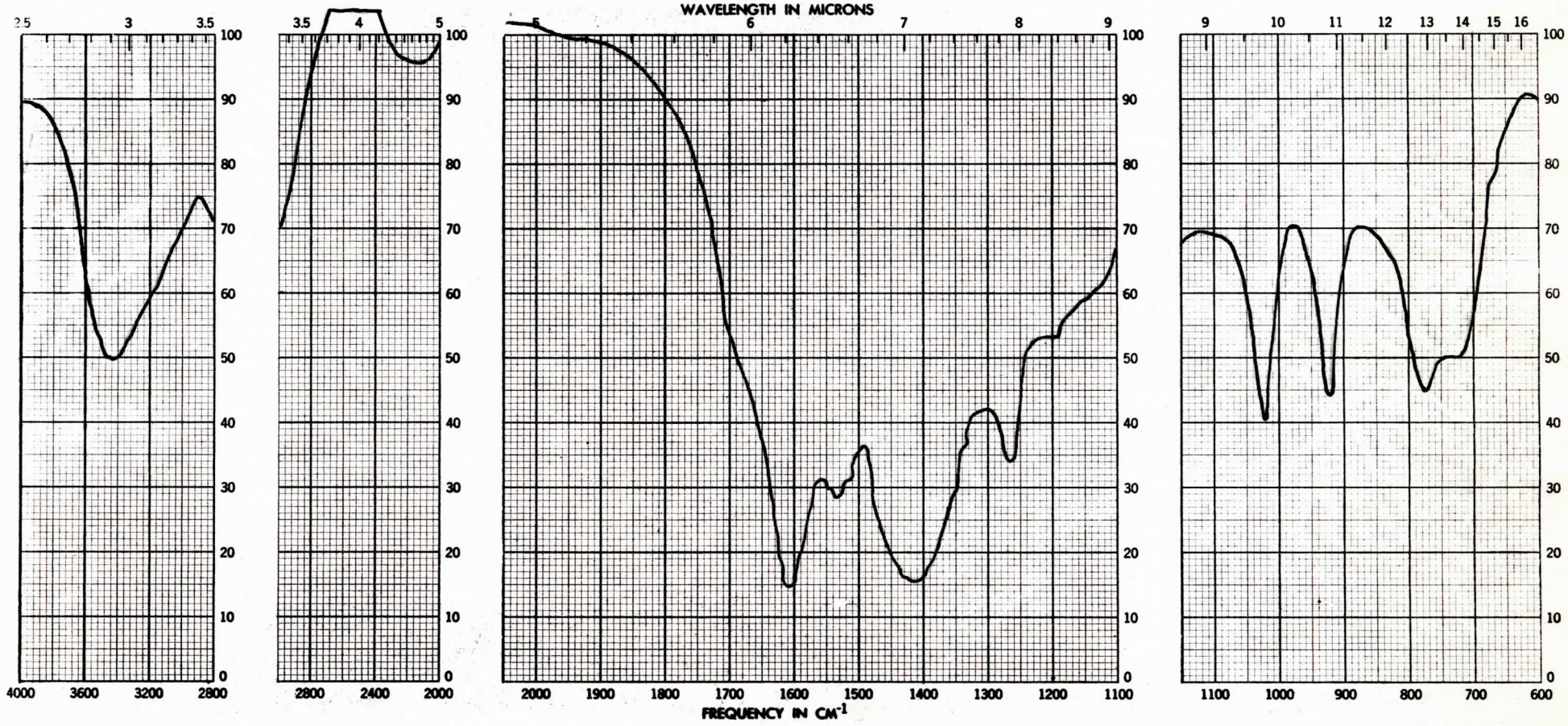


FIGURE 6

SPECTRUM OF SAMARIUM ACETYLACETONATE

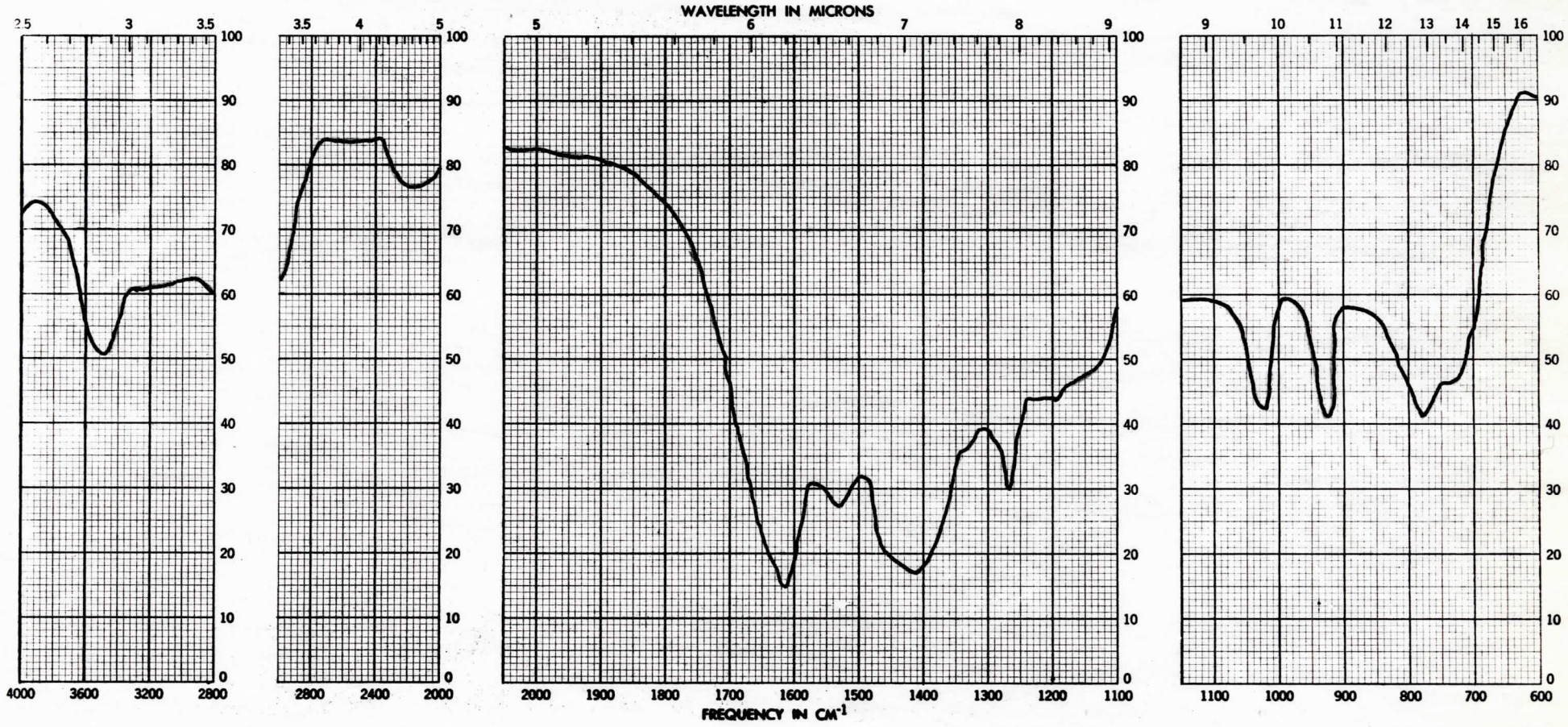


FIGURE 7

SPECTRUM OF GADOLINIUM ACETYLACETONATE

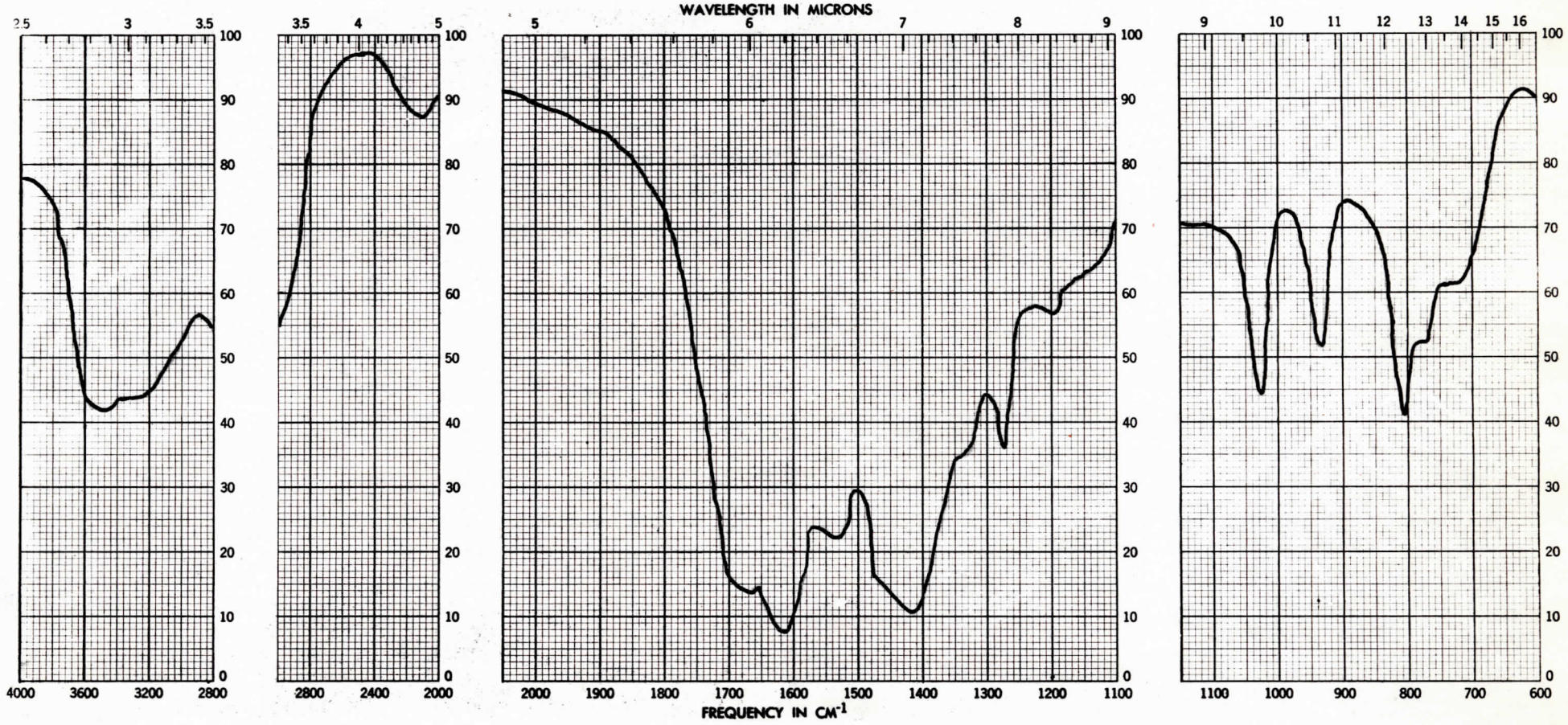


FIGURE 8

SPECTRUM OF DYSPROSIUM ACETYLACETONATE

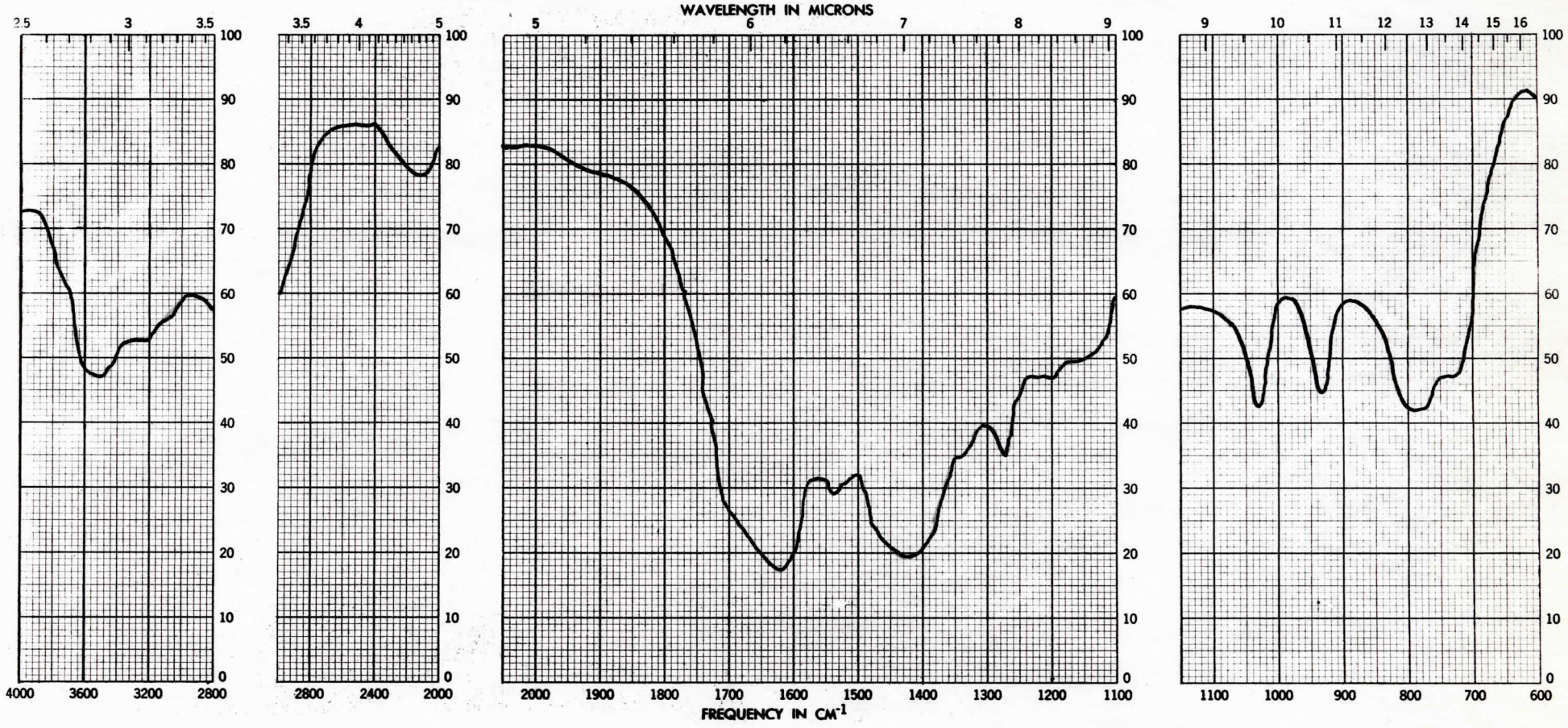


FIGURE 9

SPECTRUM OF HOLMIUM ACETYLACETONATE

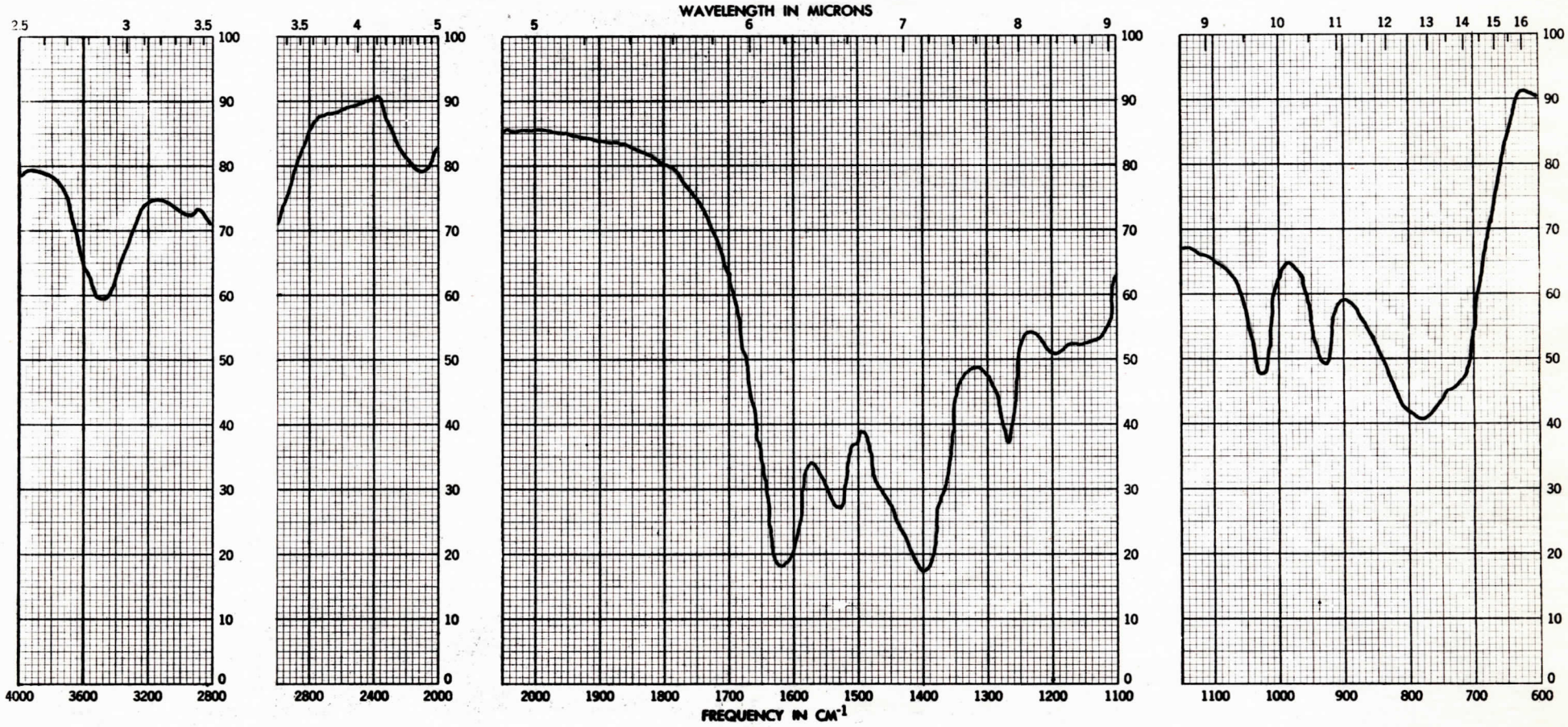


FIGURE 10

SPECTRUM OF ERBIUM ACETYLACETONATE

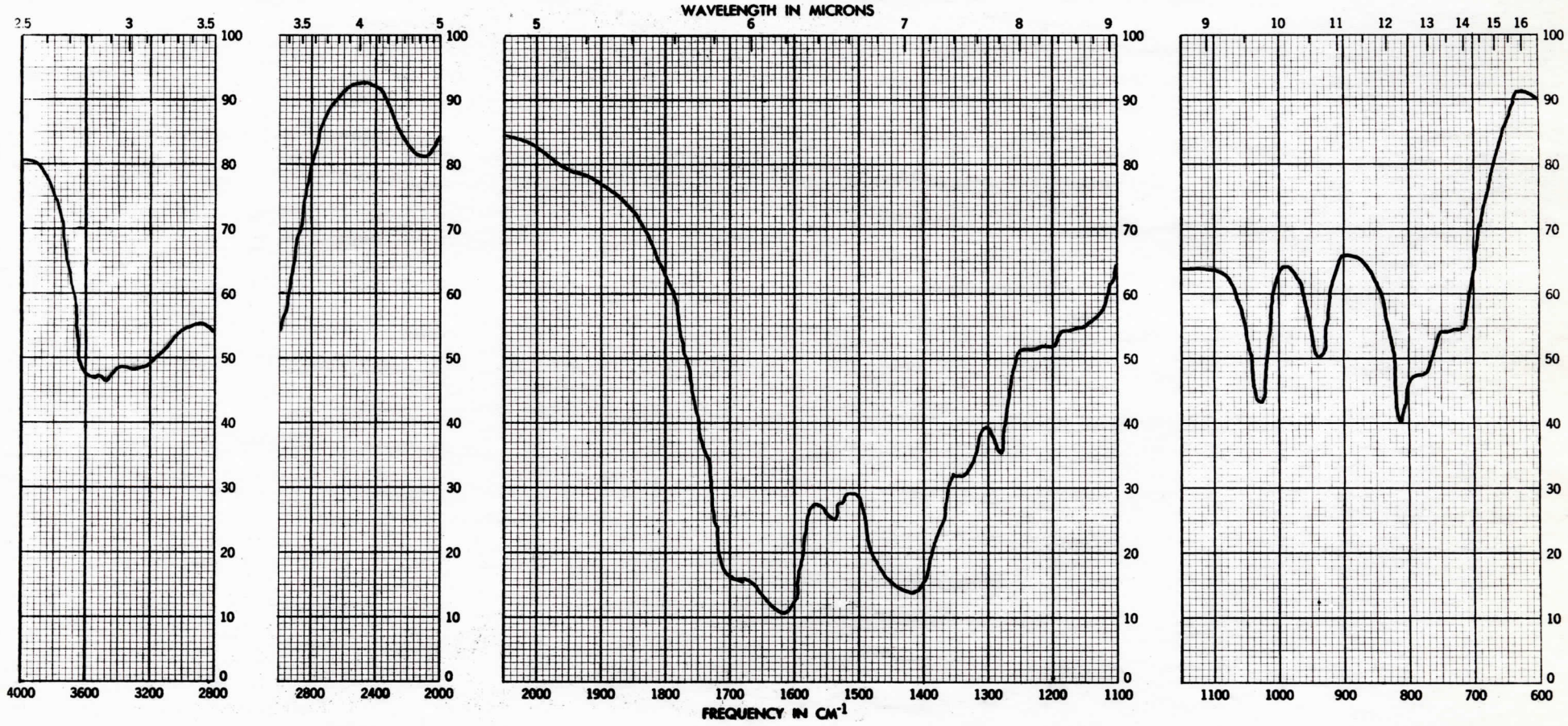


FIGURE 11

SPECTRUM OF YTTERBIUM ACETYLACETONATE

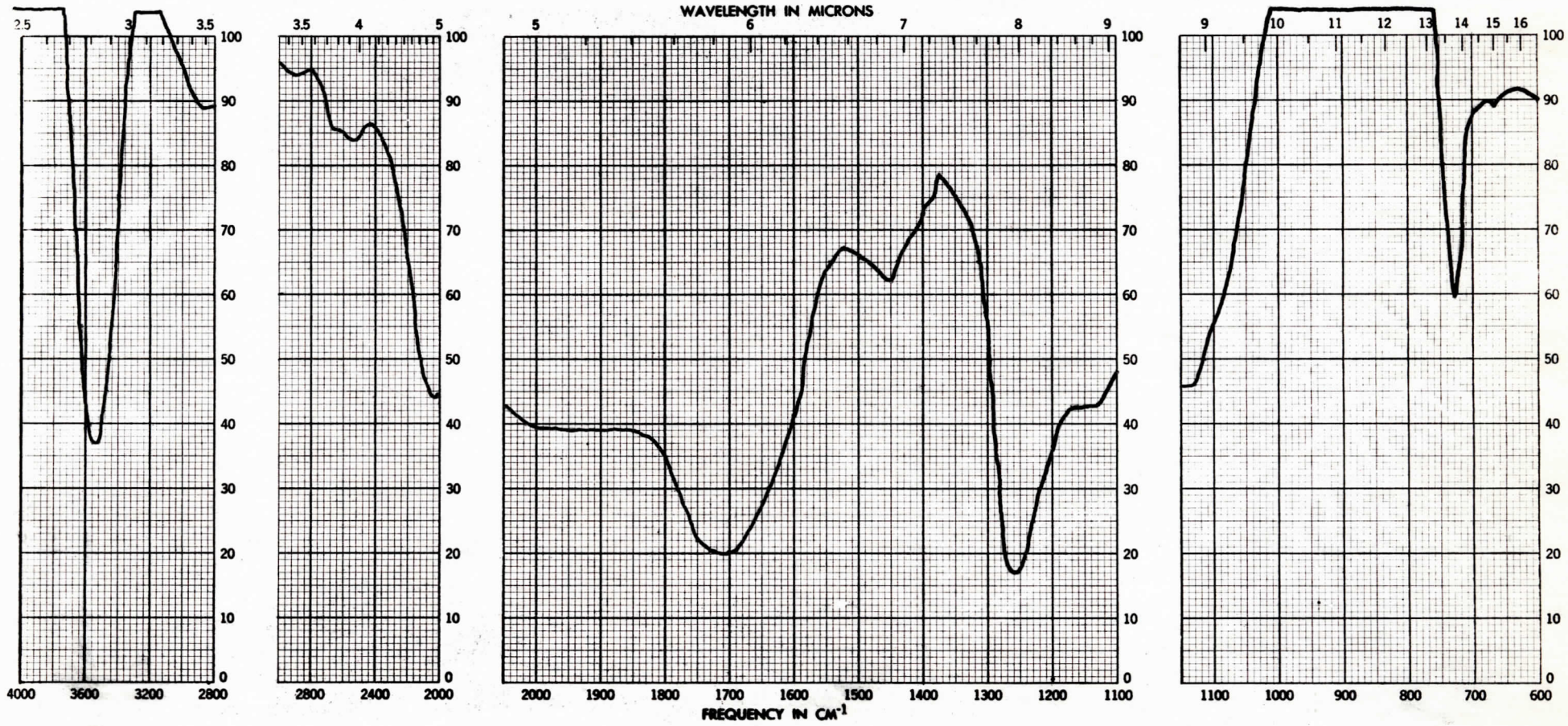


FIGURE 12

SPECTRUM OF OXALIC ACID

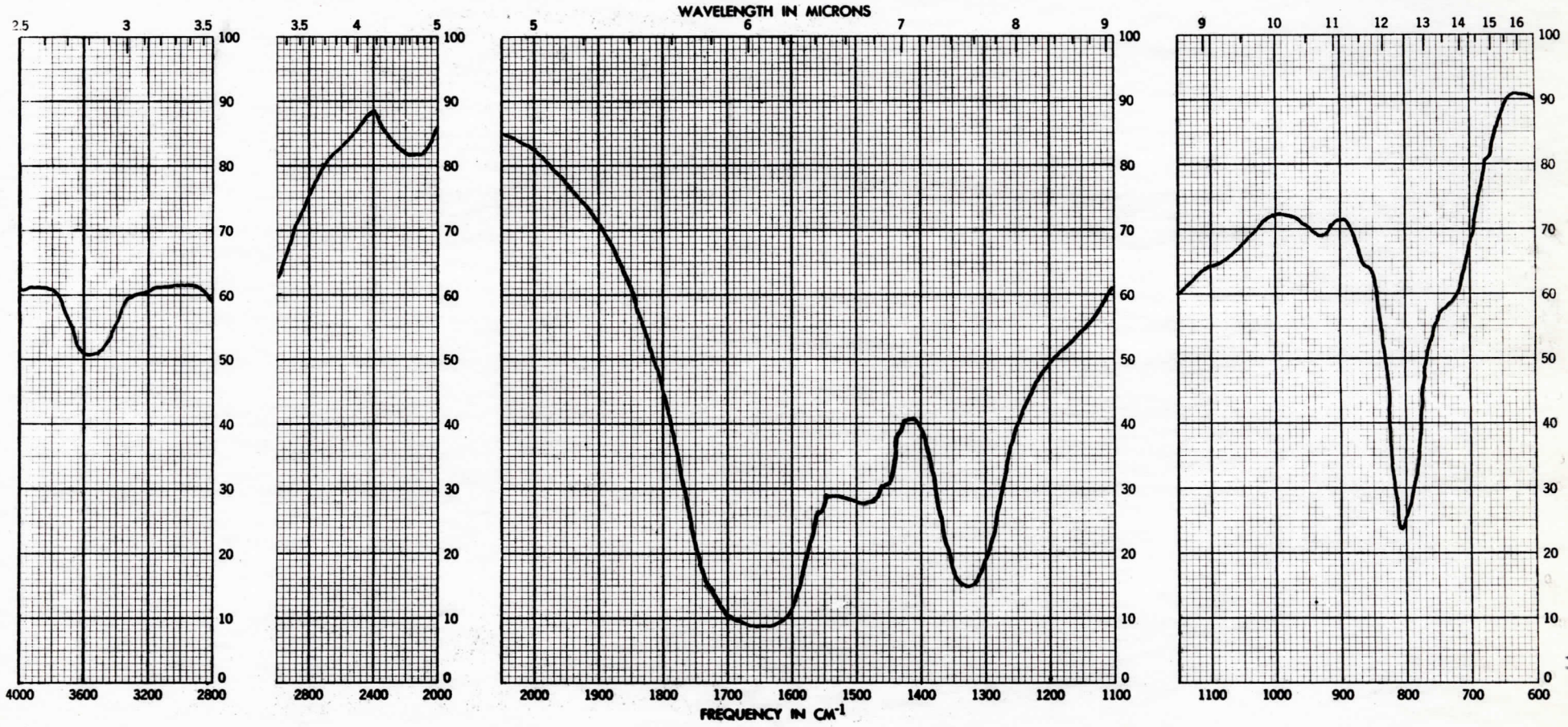


FIGURE 13

SPECTRUM OF LANTHANUM OXALATE

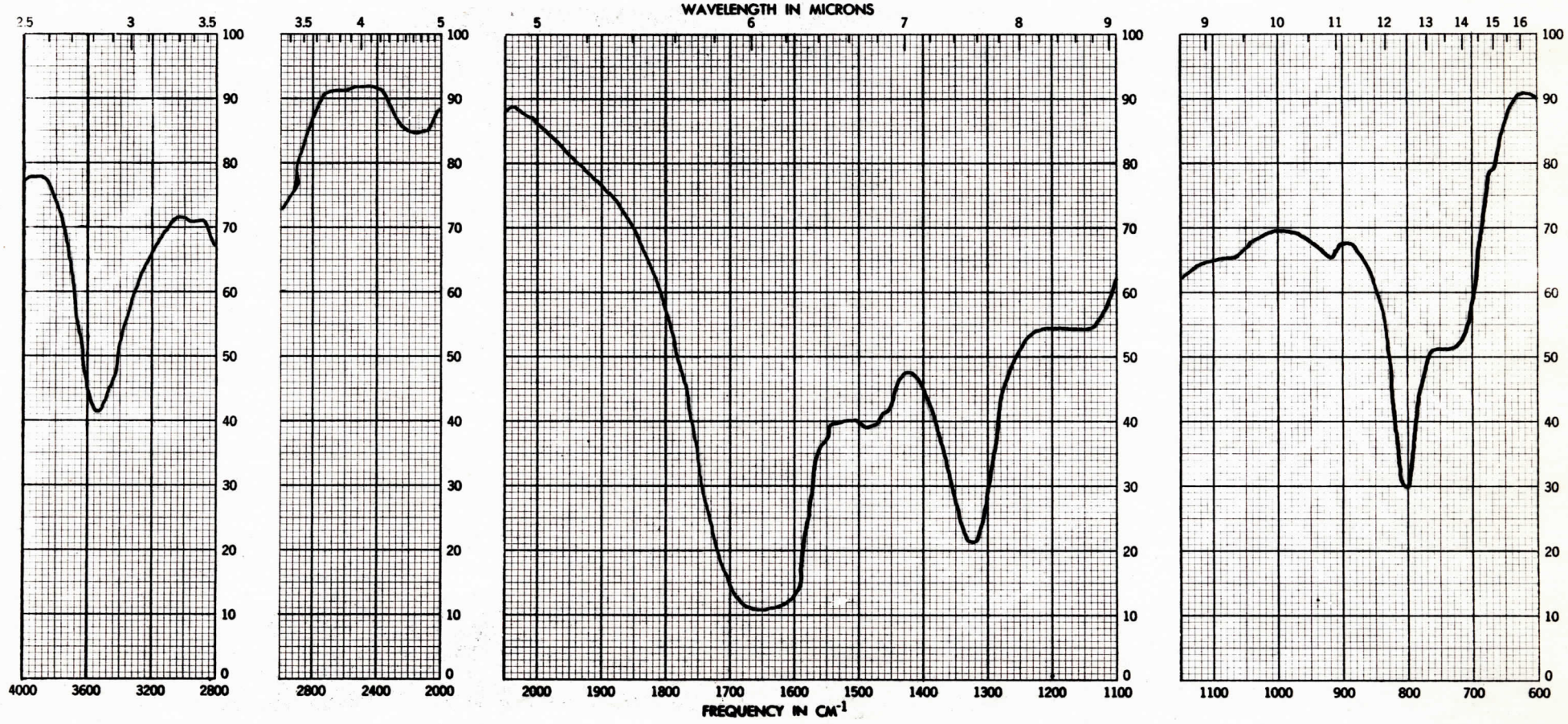


FIGURE 14

SPECTRUM OF CERIUM OXALATE

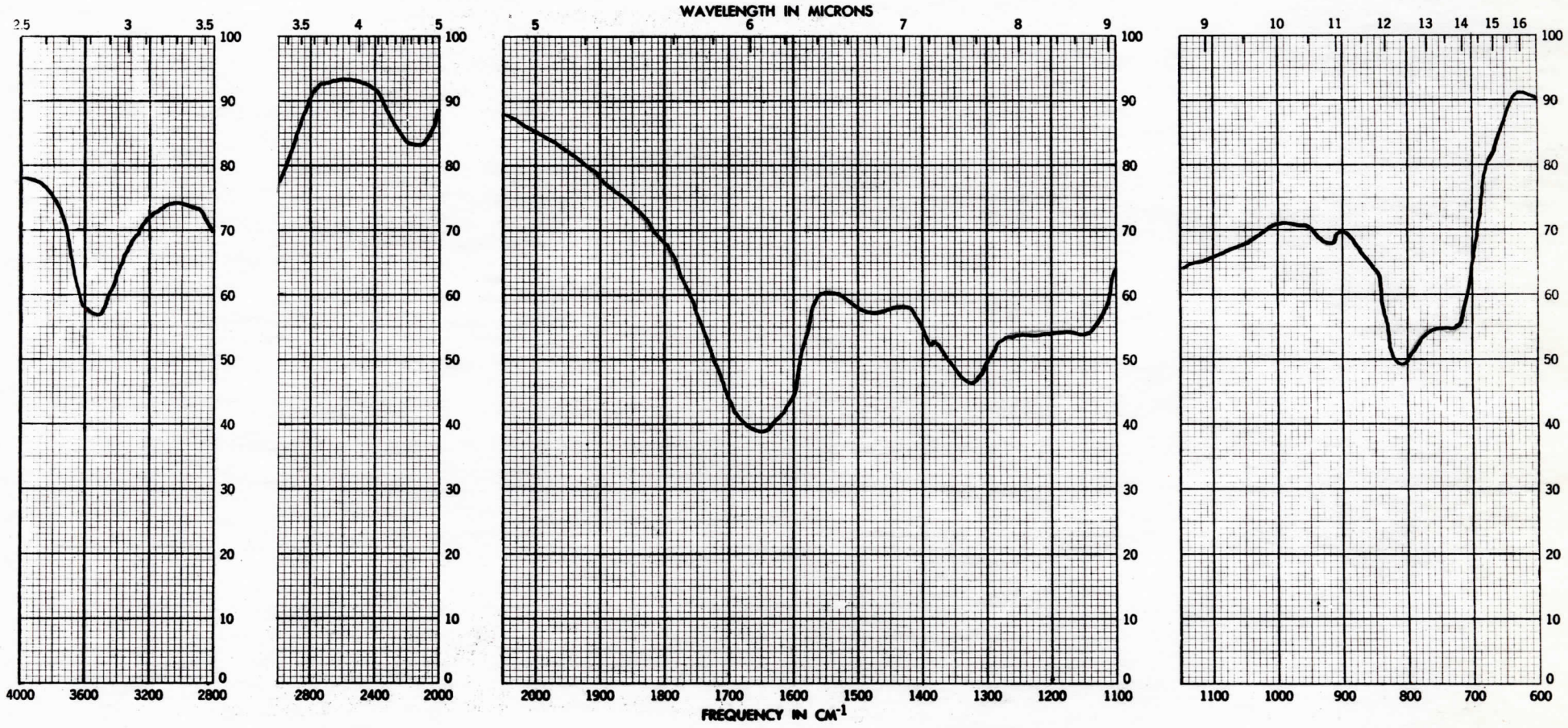


FIGURE 15

SPECTRUM OF PRASEODYMIUM OXALATE

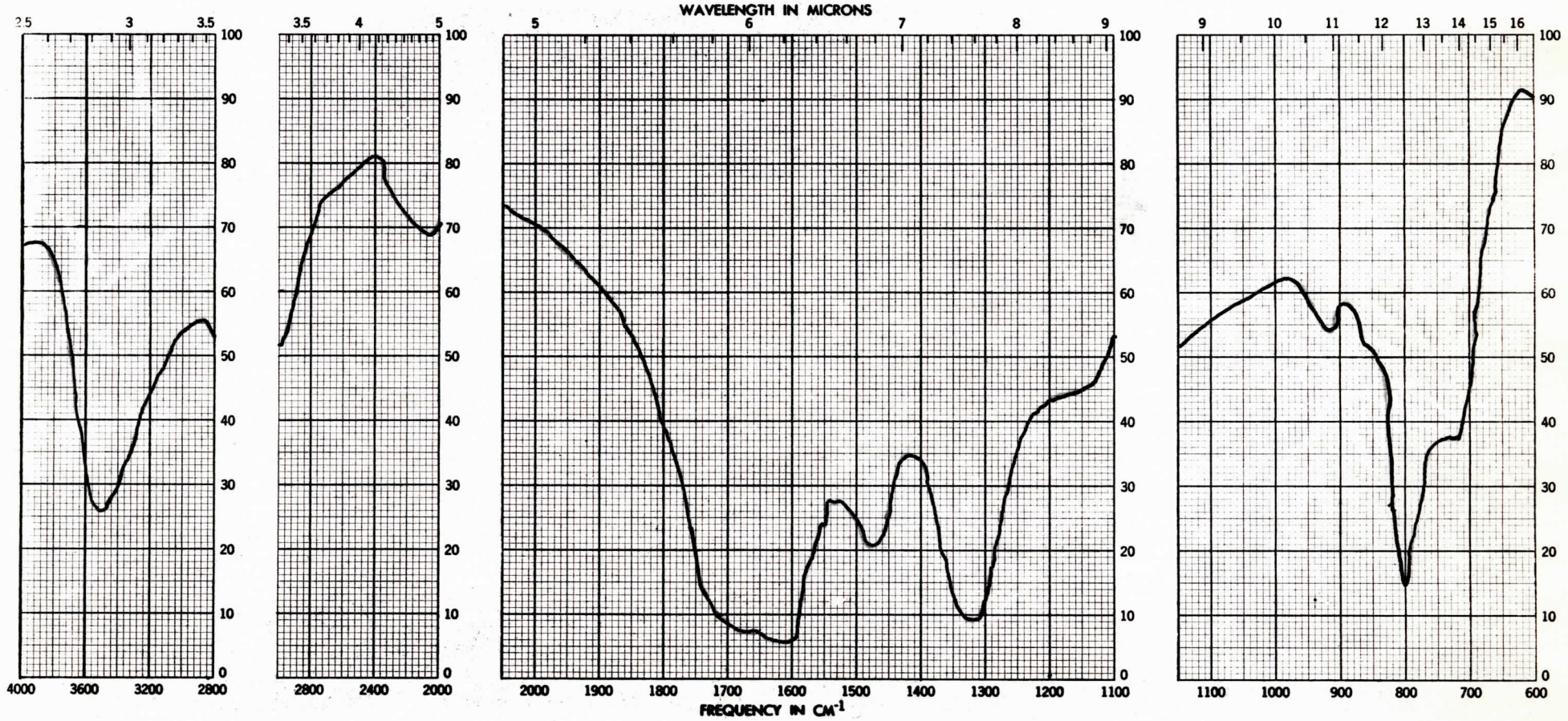


FIGURE 16

SPECTRUM OF NEODYMIUM OXALATE

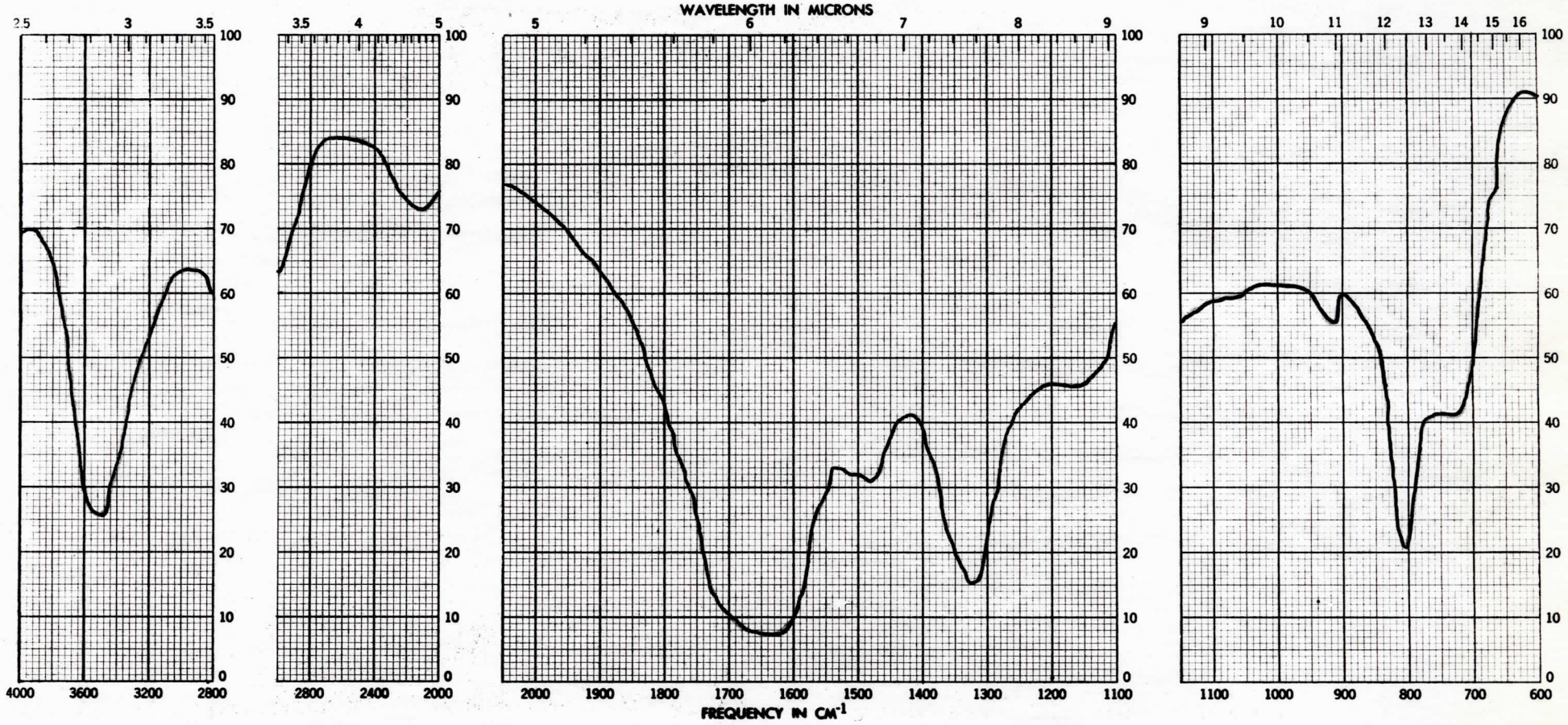


FIGURE 17

SPECTRUM OF SAMARIUM OXALATE

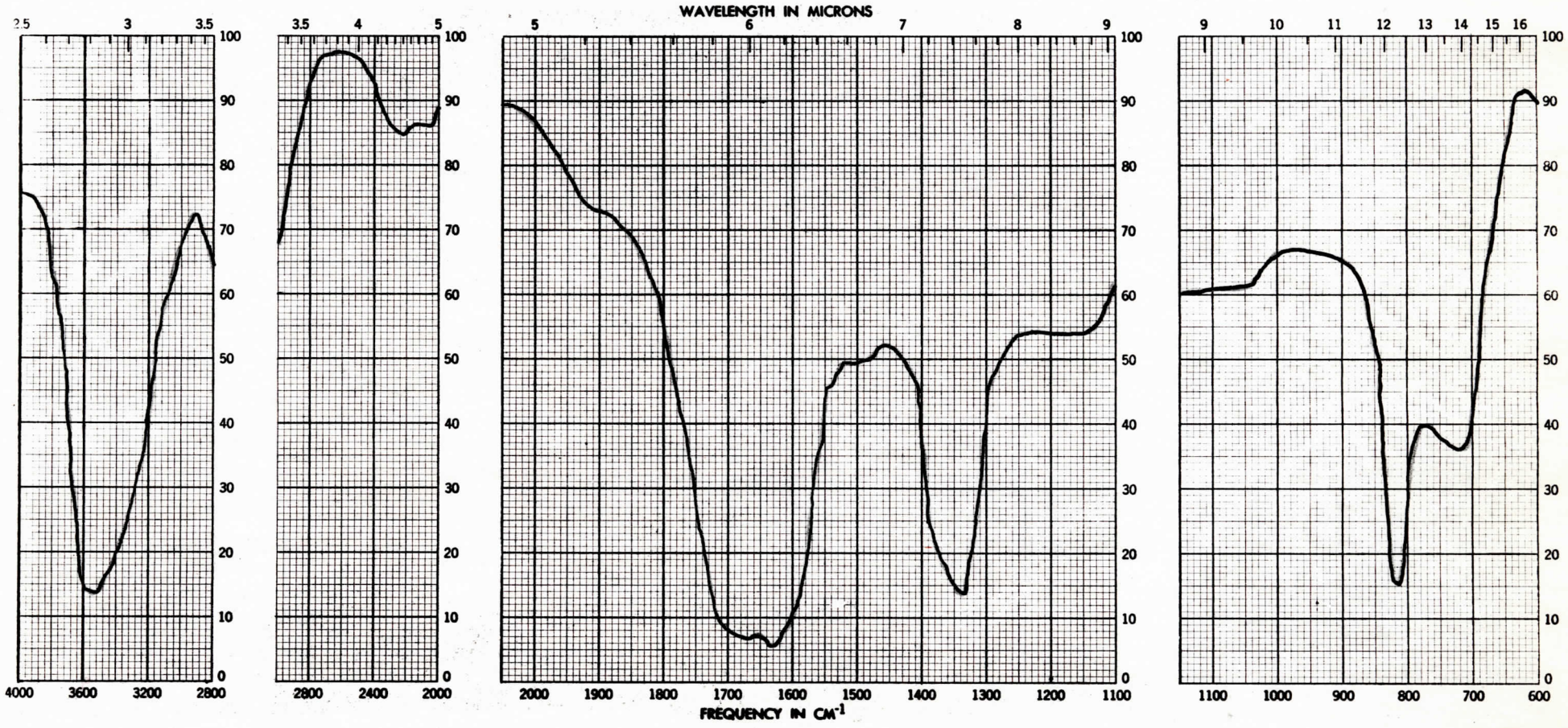


FIGURE 18

SPECTRUM OF EUROPIUM OXALATE

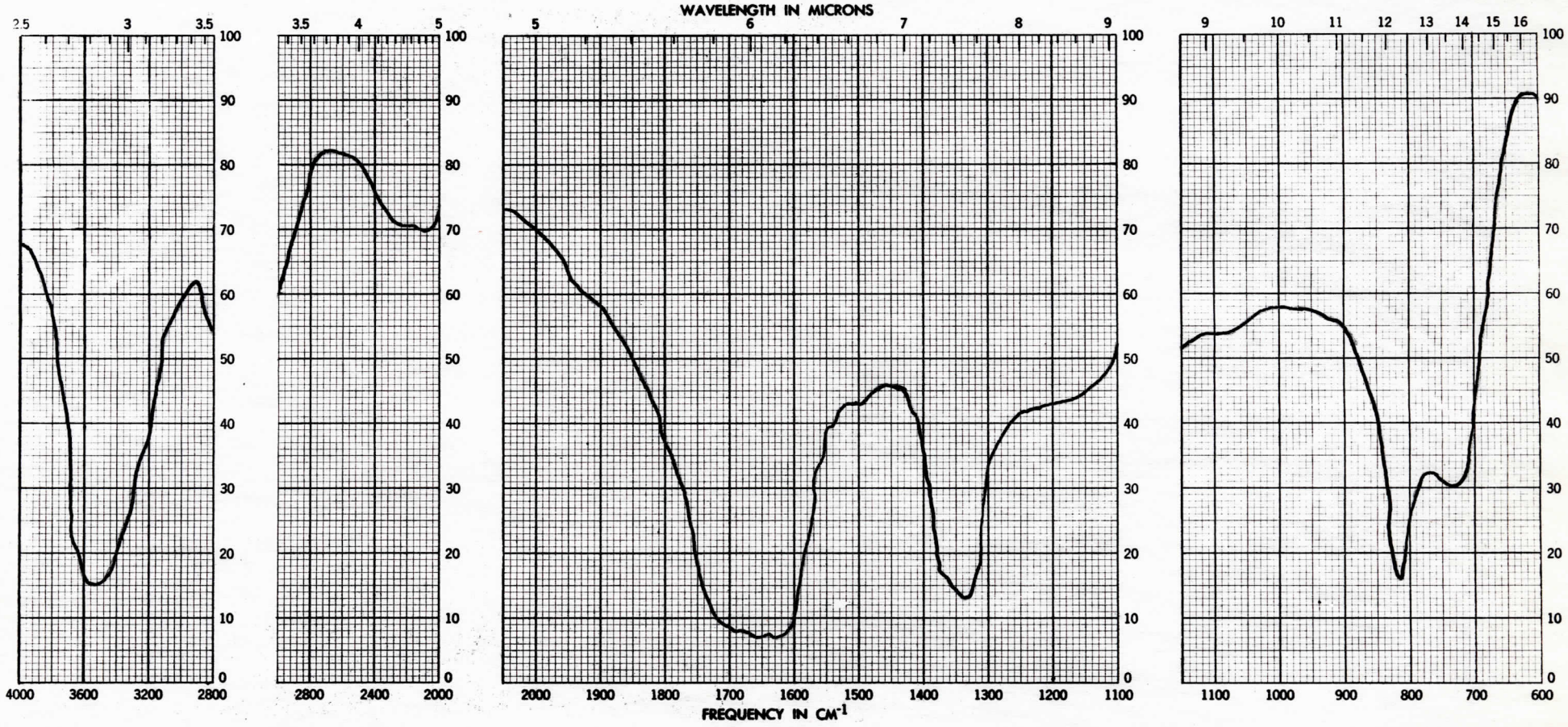


FIGURE 19

SPECTRUM OF GADOLINIUM OXALATE

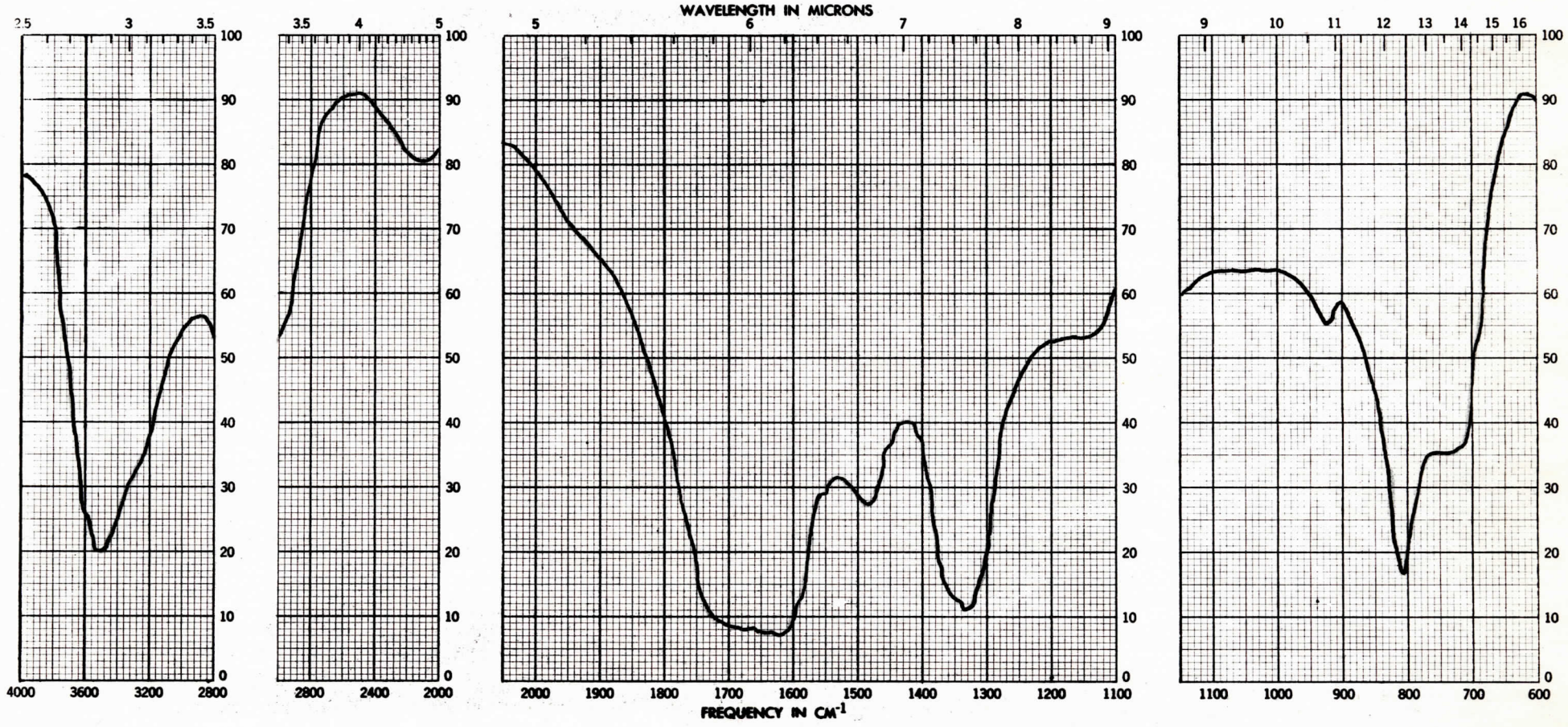


FIGURE 20

SPECTRUM OF DYSPROSIUM OXALATE

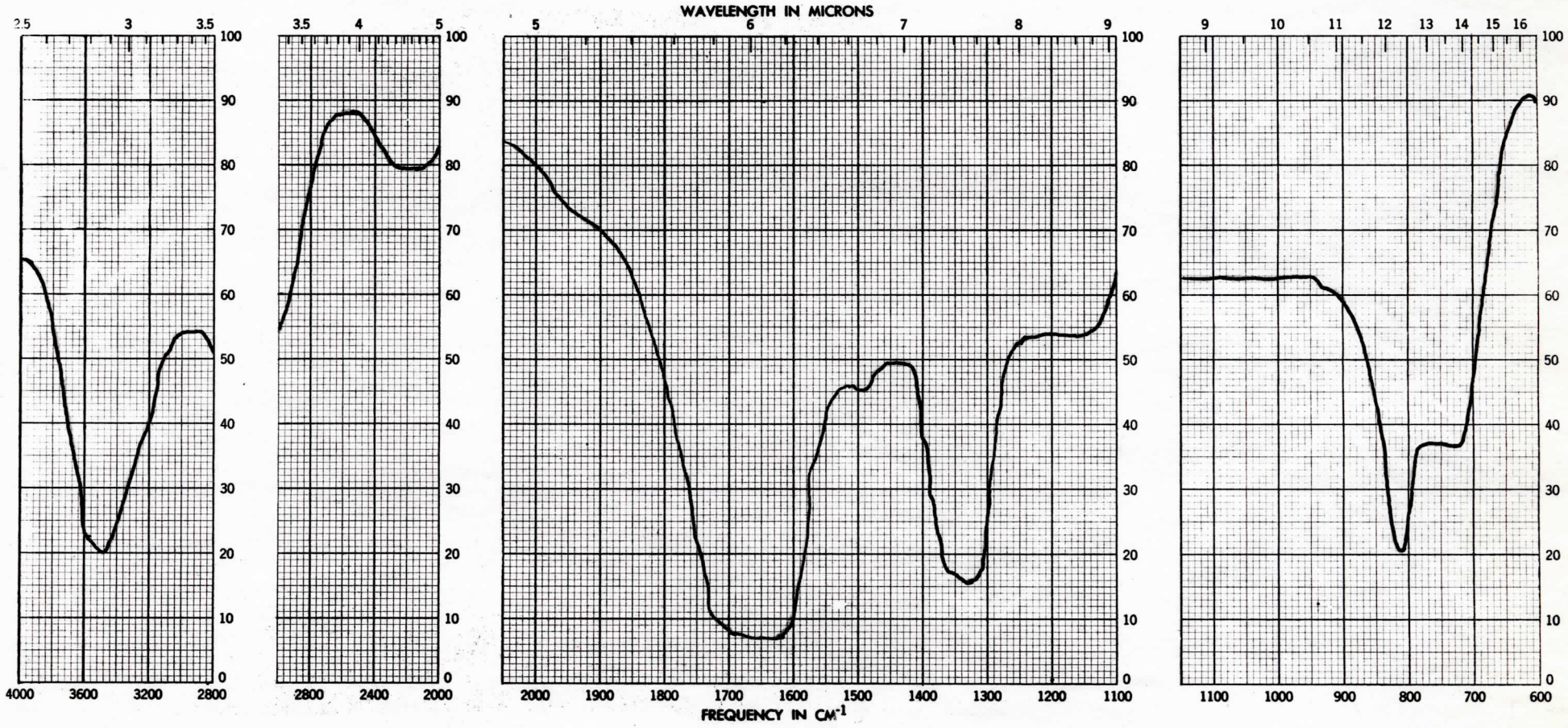


FIGURE 21

SPECTRUM OF HOLMIUM OXALATE

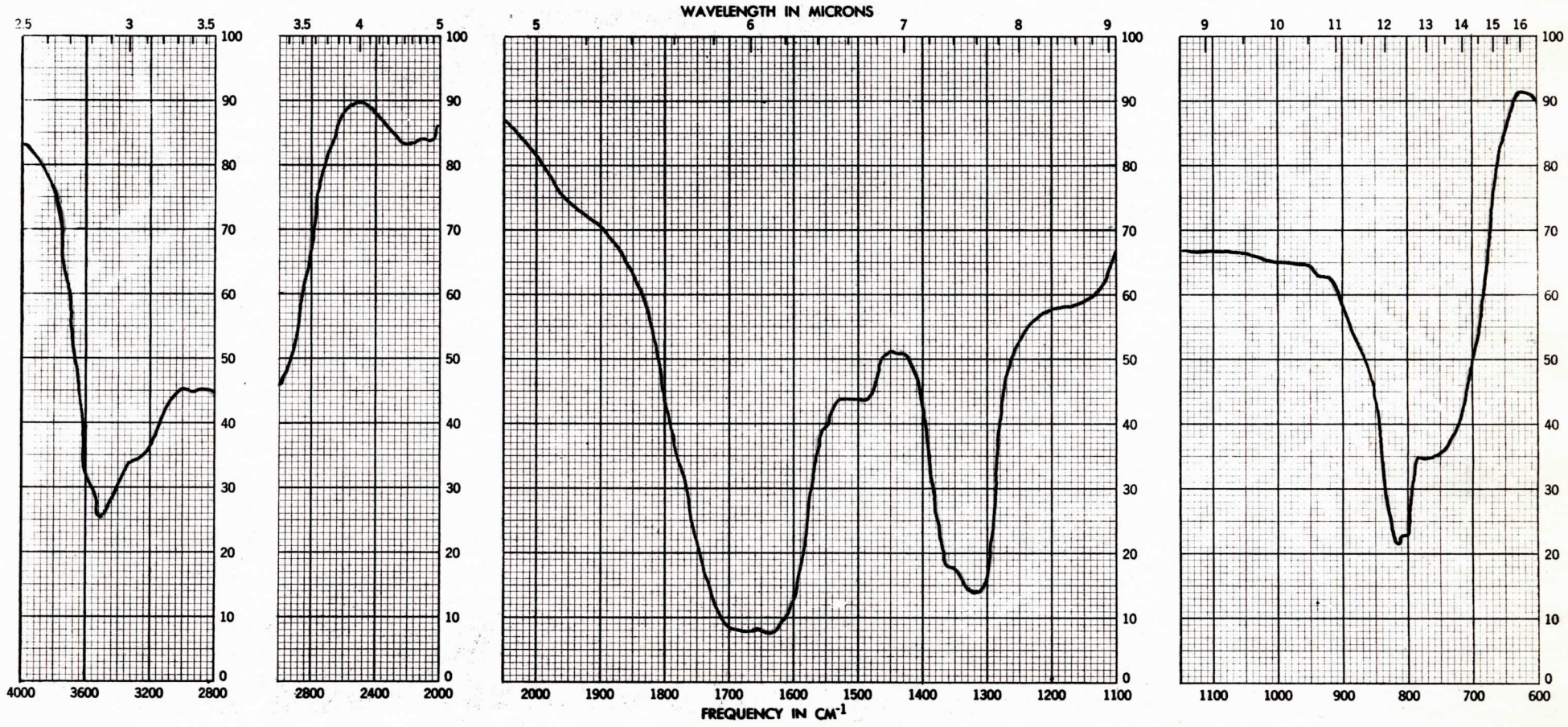


FIGURE 22

SPECTRUM OF ERBIUM OXALATE

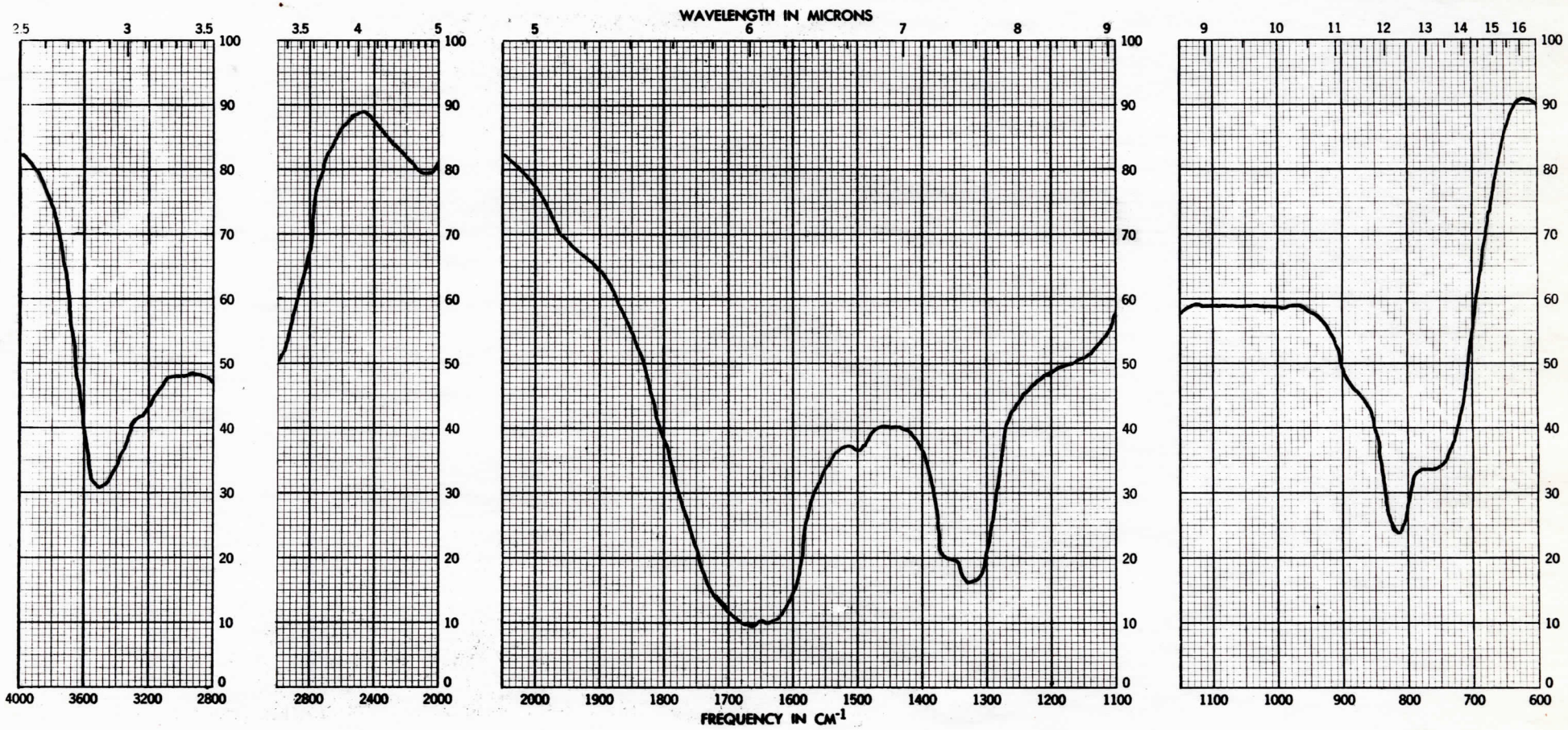


FIGURE 23

SPECTRUM OF YTTERBIUM OXALATE

TABLE III

BANDS INDEXED WITH THEIR PARTICULAR ABSORPTION ASSIGNMENTS FOR THE COMPOUNDS STUDIED

Acetylacetone		Lanthanum Acetylacetonate	
Wavenumbers (cm^{-1})	Per cent	Wavenumbers (cm^{-1})	Per cent
830	6	740	44
915	63	765	55
960	52	785	55
1003	45	927	62
1173	44	1023	67
1252	79	1200	47
1363	79	1267	71
1425	83	1415	83
1620	88	1610	83
1715	64	2200	4
3010	17	3440	58

Cerium Acetylacetonate		Praseodymium Acetylacetonate	
Wavenumbers (cm^{-1})	Per cent	Wavenumbers (cm^{-1})	Per cent
730	33	735	44
770	36	767	47
927	38	927	45
1027	40	1028	49
1200	32	1200	44
1266	49	1265	57
1405	70	1405	68
1540	56	1537	56
1608	70	1610	68
2200	0	2200	5
3480	33	3480	43

TABLE III(continued)

Neodymium Acetylacetonate		Samarium Acetylacetonate	
Wavenumbers (cm^{-1})	Per cent	Wavenumbers (cm^{-1})	Per cent
730	51	730	40
770	56	767	45
927	58	924	46
1027	61	1023	50
1210	48	1212	37
1263	66	1265	56
1410	81	1410	75
1537	69	1536	62
1610	81	1610	76
2160	8	2160	00
3460	54	3440	40

Gadolinium Acetylacetonate		Dysprosium Acetylacetonate	
Wavenumbers (cm^{-1})	Per cent	Wavenumbers (cm^{-1})	Per cent
740	43	735	29
780	49	780	38
927	49	804	49
1027	48	932	39
1220	46	1028	46
1267	60	1200	33
1410	73	1274	54
1535	63	1415	80
1615	75	1535	68
2160	14	1615	83
3500	40	1685	76
		2110	3
		3520	48

TABLE III(continues)

Holmium Acetylacetonate		Erbium Acetylacetonate	
Wavenumbers (cm^{-1})	Per cent	Wavenumbers (cm^{-1})	Per cent
740	43	740	44
785	48	785	49
928	45	928	40
1028	48	1025	43
1215	43	1200	39
1273	55	1272	53
1420	71	1400	73
1537	61	1535	63
1615	73	1622	72
2120	12	2120	10
3525	43	3490	31

Ytterbium Acetylacetonate		Oxalic Acid	
Wavenumbers (cm^{-1})	Per cent	Wavenumbers (cm^{-1})	Per cent
740	36	730	31
785	42	1150	47
809	50	1260	73
935	40	1450	28
1030	47	1712	70
1200	39	2540	6
1280	54	3540	53
1420	76		
1538	65		
1620	79		
1685	74		
2100	9		
3530	43		

TABLE III(continued)

Lanthanum Oxalate		Cerium Oxalate	
Wavenumbers (cm^{-1})	Per cent	Wavenumbers (cm^{-1})	Per cent
805	66	740	38
930	21	805	60
1325	75	920	25
1490	63	1325	69
1650	81	1475	51
2120	8	1648	79
3560	39	2140	5
		3540	49

Praseodymium Oxalate		Neodymium Oxalate	
Wavenumbers (cm^{-1})	Per cent	Wavenumbers (cm^{-1})	Per cent
740	36	740	53
810	41	800	76
925	22	920	37
1325	44	1328	81
1475	33	1475	69
1650	51	1630	84
2120	7	2080	21
3540	34	3500	64

TABLE III(continued)

Samarium Oxalate		Europium Oxalate	
Wavenumbers (cm^{-1})	Per cent	Wavenumbers (cm^{-1})	Per cent
750	49	720	54
805	70	815	75
920	35	1338	77
1325	75	1650	84
1480	59	2280	5
1645	83	3520	76
2080	17		
3520	64		

Gadolinium Oxalate		Dysprosium Oxalate	
Wavenumbers (cm^{-1})	Per cent	Wavenumbers (cm^{-1})	Per cent
730	59	750	55
818	75	810	74
1340	77	925	35
1640	84	1330	79
2120	20	1485	63
3540	75	1650	83
		2080	10
		3520	70

TABLE III (continued)

Holmium Oxalate		Erbium Oxalate	
Wavenumbers (cm^{-1})	Per cent	Wavenumbers (cm^{-1})	Per cent
769	53	770	55
815	70	815	68
1330	74	1317	76
1485	45	1350	72
1650	83	1490	47
2160	10	1660	82
3520	20	2160	6
		3500	65

Ytterbium Oxalate	
Wavenumbers (cm^{-1})	Per cent
765	56
815	66
1320	74
1350	71
1390	53
1650	80
2080	10
3490	60

TABLE IV

ASSIGNMENT OF CERIUM BANDS

Cerium Oxalate		Cerium Acetylacetonate	
Wavenumbers (cm)	Assignment	Wavenumbers (cm)	Assignment
740	?	730	?
805	O—C—O str	770	C—H out of plane bend
920	C—C str		
1325	C—O str	927	CCH_3 + CO str
1475	C—H d	1027	CH_3 rock
1648	C—O	1200	C—H in plane bend
2140	?		
3540	M—O str	1266	C—C str and CCH_3 str
		1405	CH_3 deg def
		1540	C—O str
		1608	C—C str
		2200	?
		3480	?

CHAPTER V

SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

I. SUMMARY

The acetylacetonates of La, Ce, Pr, Nd, Sm, Gd, Dy, Ho, Er, and Yb, were prepared. In addition, the oxalates La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, and Yb were obtained. Infrared spectra of these complexes have been obtained with a Beckmann Infrared Spectrophotometer, IR-7 in the region from 600-4000 cm^{-1}. The absorption effects of each complex have been indexed with respect to frequencies and relative intensities. The results show that no significant differences of frequencies were observed for either the oxalates or acetylacetonates of the lanthanides.

II. CONCLUSION

It may be concluded from this study that no changes in the metal ion-ligand bond length occurred as a result of changing the metal ion for the rare earth elements.

It is further concluded the changes in absorption spectra of these lanthanide complexes do not occur in the 600 - 4000 cm^{-1} region.

III. RECOMMENDATIONS

Intensity bands of the acetylacetonates should be investigated for the purpose of finding a correlation between the change in metal ion and change in intensity.

Also, the rare earth acetylacetonates should be scanned in the infrared region between 600 and 200 cm^{-1} to explore the possibility of finding a metal-oxygen stretching vibration which can be correlated to the change in metal ion.

The variations of intensity imply differences in molecular packing and therefore possible differences in crystal structures. Therefore, it is suggested that x-ray diffraction studies be made on these complexes.

AN INVESTIGATION OF THE INFRARED SPECTRA OF THE RARE EARTH ACETYLACETONATES AND OXALATES

By

Terry Lester Morris

The purpose of this study was to prepare a number of rare earth acetylacetonates and oxalates, to obtain the infrared spectra of these compounds, and to determine the effect on the spectra brought about by changing the metal ion.

The complexes were prepared by standard methods. The acetylacetonates were prepared by the addition of a water solution of acetylacetone to the corresponding nitrate of the rare earth (15). The oxalates were prepared by adding the nitrate of the particular rare earth to a saturated solution of oxalic acid (16).

Infrared spectra were obtained for all of the compounds in the form of potassium bromide pellets. Infrared absorption bands of oxalic acid, acetylacetone, and the lanthanide complexes were indexed with respect to wavenumbers and absorption.

The study provided the following conclusions:

1. The metal ion of the complex does not alter the frequencies of the bands in rare earth acetylacetonates and oxalates in the infrared region between 600 and 4000 cm^{-1}.

2. It is further concluded on the basis of these results that detection of differences in various rare earth acetylacetonates or oxalates in this region of the infrared spectrum is not possible.

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